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Solvent effects in the hydrogenation of 2-butanone

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1. Introduction

The ability of a solvent to influence either the rate or selectivity of a reaction has been known within organic chemistry for 150 years [1]. Over that time there have been a number of attempts to understand the role of the solvent with methods including multiple linear regression analysis, factor analysis and principal component analysis all being used in an attempt to develop some level of understanding and predictability of these effects. Such analysis tends to rely on various free energy relationships, and despite the complicated nature of solvents and solutions, they have shown that they can provide some insight into many chemical processes [1].

Like the organic reactions above, many heterogeneously catalysed processes are carried out in a solvent for the simple purpose of dissolving the reactants and keeping the products in solution. Here too, solvents are known to influence both rate and selectivity although in such systems the multi-phase nature of the reactions increases their complexity. Therefore, in addition to factors such as solvent polarity, dielectric constant and acid/base properties of the reaction medium, factors such as the solvation of reactants

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ABSTRACT

In liquid-phase reaction systems, the role of the solvent is often limited to the simple requirement of dissolving and/or diluting substrates. However, the correct choice, either pure or mixed, can significantly influence both reaction rate and selectivity. For multi-phase heterogeneously catalysed reactions observed variations may be due to changes in mass transfer rates, reaction mechanism, reaction kinetics, adsorption properties and combinations thereof. The liquid-phase hydrogenation of 2-butanone to 2butanol over a Ru/SiO₂ catalyst, for example, shows such complex rate behaviour when varying water/ isopropyl alcohol (IPA) solvent ratios. In this paper, we outline a strategy which combines measured rate data with physical property measurements and molecular simulation in order to gain a more fundamental understanding of mixed solvent effects for this heterogeneously catalysed reaction. By combining these techniques, the observed complex behaviour of rate against water fraction is shown to be a combination of both mass transfer and chemical effects.

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and products, gas solubility and other mass transfer effects need to be considered as these can all significantly influence reaction rates and product selectivities [2]. Other important criteria for consideration include the potential for improved heat transfer and the influence on deactivation such as reduced carbon laydown on the catalyst surface [3].

Toukonitty et al. for example investigated solvent effects for the enantioselective hydrogenation of 1-phenyl-1,2-propanedione with a cinchonidine modified Pt/Al₂O₃ catalyst [4]. When using a range of different solvents, including binary solvent mixtures, it was observed that while no correlation between the solvent dielectric constant and hydrogenation rate could be found the enantiomeric excesses decreased non-linearly with an increasing solvent dielectric constant. This dependence was partly attributed to the open (3) cinchonidine conformer, although it was primarily taken into account by applying transition state theory and the Kirkwood treatment with the result that a model was able to predict the behaviour of the system as a function of the solvent dielectric constant. Contrasting with this work, Mukherjee and Vannice later reported on solvent effects during the liquid-phase hydrogenation of citral using Pt/SiO₂ and eight nonreactive solvents [5]. Here it was observed that the rates were affected by the choice of solvent; however, differences in the product distribution were not significant. In this case, it was found that the variation in specific activity





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did not correlate with either the solvent dielectric constant or the dipole moment. Similarly, Gómez-Quero et al. studied solvent effects during the liquid-phase hydrodehalogenation of haloarenes in methanol, THF, water/methanol and water/THF mixtures using a Pd/Al₂O₃ catalyst [6]. Within this work they noted that higher initial rates were observed with increasing water content in the solvent mixture and attributed this to an increase in the dielectric constant of the medium. Such observations were consistent with an electrophilic mechanism in which the solvent helped to stabilise the arenium intermediate. An overall dependence of rate on solvent for this reaction could then be established with approximately 80% of the contribution being due to the dielectric constant with molar volume being a secondary factor. Mixed alcohol/water solvents, the subject of this work, have also been investigated previously. For example, a minimum in the rate of 2-butene-1,4-diol hydrogenation (the second step in the hydrogenation of 2butyne-1,4-diol over Pd/Al₂O₃) occurred at 80-90 mol_{H2O}% in a 2-propanol/water solvent [7]. Elsewhere, an enhancement in the rate of reaction in mixed alcohol/water solvents as compared to the pure alcohol has been observed in 2-butanone hydrogenation over Pd catalysts [8]; acetophenone hydrogenation over Raney-Ni [9]; and o-nitrotoluene hydrogenation over Pd/C [10]. In the latter example, an increase of almost 50% in the reaction rate was reported upon changing solvent from pure methanol to a mixed methanol/water solvent containing 18% water.

As mentioned above, other factors are also important, for example, polar solvents are known to enhance the adsorption of nonpolar reactants and non-polar solvents the adsorption of polar reactants [11]. More recently, Vanoye et al. observed an interesting inflection in the initial rates obtained using a mixed ethanol/heptane solvent system for the liquid-phase dehydration of ethanol to diethylether over heterogeneous sulphonic-acid catalysts [12]. In this case, the authors concluded that the observed inflection in non-polar solvents could be explained by the formation of a new liquid phase around the acid site indicating that local structure is also important. It is quite clear from the above discussion that the role of the solvent is less well defined than in normal organic reactions with increases in rate being observed in some systems, and selectivity in others.

In briefly reviewing selective hydrogenation reactions over ruthenium catalysts which relate to the work discussed herein, it is further noted that carbonyl hydrogenations are particularly active in the presence of water [13]. Conversely, in the hydrogenation of benzene over Ru/C, water was found to have an adverse effect on the reaction rate [14]. Similar effects of water have also been observed by Vaidya and Mahajani in the hydrogenation of *n*-valeraldehyde to *n*-amyl alcohol over Ru/Al₂O₃; however, no explanation was given for its influence [15]. A possible reason for enhanced activity in water may be due to its ability to dissociate over different metal surfaces. The dissociation of water over Ru is well known in vapour phase studies as well as in aqueous solutions; this leads to the formation of surface hydroxyl intermediates and protons which can subsequently influence the reaction [16,17].

While such effects are known, to our knowledge there are no studies which extensively examine the role of water in a mixed solvent system covering its effect on mass transfer, diffusion and reaction kinetics. Therefore, a detailed study of the influence of water over diffusion, adsorption, desorption and elementary reaction steps is necessary to improve our current understanding of the role played by the solvent in altering reaction activity and selectivity. In this paper, we attempt to investigate such effects and have probed the role of water on the hydrogenation of 2-butanone (methyl ethyl ketone (MEK)) to 2-butanol using a combination of experiments and density functional theory. These results indicate that the rate of hydrogenation of MEK is strongly correlated to the solvent composition and that water plays an important role in altering energetics and kinetics of the elementary steps involved in the overall hydrogenation.

2. Materials and methods

Catalysts comprised of 1% and 5% Ru/SiO₂ and were prepared by incipient wetness using an aqueous ruthenium (III) chloride trihydrate salt (density 2250 \pm 100 kg m⁻³). They were dried at 393 K in air and subsequently reduced in 5% H₂/95% He at 673 K for 3 h. Kinetic experiments were carried out in a 380 ml Premex stainless steel reactor, equipped with a gas inducing impeller with online hydrogen consumption monitoring. The solvents used were ultrapure water (distilled, deionised >18 M Ω) and/or 2-propanol (Reidel De Haan >99.5%). Typically, 240 ml of solvent was charged to the reactor with the required mass of catalyst (0.1 g unless otherwise stated). After purging with N₂, the solvent was heated to the desired temperature before injection of 7.5 ml 2-butanone (Aldrich 99+%) and 2.5 ml solvent (2-butanone concentration of 0.33 mol l^{-1}). After purging with H₂, the reactor was pressurised and monitored by hydrogen consumption or by sampling using a GC equipped with a DB-1 capillary column and FID detector. All gases were BOC research grade. Mass balances performed on reactions were >95% in all cases.

Pulsed field gradient (PFG) NMR measurements of diffusion coefficients were conducted using a Diff30 diffusion probe with a 10 mm r.f. coil on a Bruker DMX 300 spectrometer, operating at a ¹H resonance frequency of 300.13 MHz. Samples were prepared using 5 mm NMR tubes filled to a height of approximately 20 mm. The PGSTE pulse sequence was employed with the diffusion encoding time Δ and gradient pulse duration δ fixed at 100 ms and 2 ms, respectively, with a maximum gradient strength, g, of up to 1 T/m [18]. All measurements were carried out at 303.15 K.

THz Time-Domain Spectroscopy (THz-TDS) studies were carried out using coherent pulses of broadband terahertz radiation (0.1-4 THz) generated by photoexcitation of a DC biased semiinsulating GaAs substrate by 12 fs pulses of a NIR laser (Femtolasers, Femtosource cM1, Vienna, Austria, centre wavelength 800 nm). In order to suppress the absorption of water vapour in the air, the sealed sample chamber was purged by nitrogen gas to ensure a relative humidity below 2% for all measurements. Liquid samples were measured in a standard cell (PIKE Technologies, Watertown, USA) comprising 3 mm z-cut quartz windows and a 200 μ m PTFE spacer. For each sample, 200 time-domain waveforms were collected and averaged.

Periodic gradient-corrected density functional theoretical (DFT) [19] calculations as implemented in the Vienna *ab initio* Simulation Package (VASP) [20] were used to follow the reaction energies and activation barriers for different pathways involved in the hydrogenation of MEK over a model Ru(0001) surface and to simulate the effects of the solvent. The Kohn-Sham equations were solved using a plane-wave basis set with a cut-off energy of 400 eV [21]. The Perdew-Wang 91 exchange correlation functional was used to describe non-local gradient corrections [22]. The core electrons and the nuclei of the atoms were described by Vanderbilt ultrasoft pseudopotentials [23]. A $3 \times 3 \times 1$ *k*-point grid was used to model the first Brillouin zone [24]. All the reported calculations were carried out spin-restricted. The wavefunctions were converged to within 1×10^{-4} eV and the geometries were optimised until the force on each atom was less than 0.05 eV/Å. In order to test the degree of accuracy, we tightened the electronic convergence criterion from 10^{-4} to 10^{-6} eV and the structural optimisation criterion from 0.05 to 0.01 eV/Å and found that the energies for the adsorption of hydrogen and methyl ethyl ketone on Ru(0001) changed by less than 0.002 eV and 0.03 eV, respectively. As such, we have used

the lower criterion to carry out the calculations reported herein. Transition states were isolated using the climbing nudged elastic band approach, which optimises the forces on all of the atoms for a particular image and over a series of images chosen along the minimum energy path until the force perpendicular to the reaction coordinate was within 0.05 eV/Å [25]. Frequency calculations were carried out for each transition state to ensure that there was a single imaginary frequency corresponding to vibration mode along the reaction coordinate. In the transition state calculations in the presence of a solvent, the solvent molecules are allowed to move along the reaction coordinate. This enables us to model the possible stabilisation of transition state by the solvent molecules.

The Ru(0001) surface was modelled by using a 3×3 unit cell comprised of four metal layers along with 16 Å vacuum spacing normal to the metal surface to separate the metal slabs. The aqueous medium was simulated by filling the vacuum region within the unit cell with 24 water molecules in order to simulate a density of water of 1 g/cm³. The initial starting structures were adapted from previous long time (30 ps) ab initio molecular dynamic simulations carried out for water on Cu(111) and Pt(111) [45]. For the reaction carried out in 2-propanol, 6 isopropyl alcohol (IPA) molecules were used in order to create a density of 0.785 g/cm³. The initial structure of the solvent, represented by explicit solvent molecules, was obtained by carrying out a series of simulated annealing runs using ab initio molecular dynamics (AIMD) as implemented in VASP. The AIMD simulations (at 400 K, $\Delta t = 1$ fs) were performed for both systems within an NVT ensemble to obtain an optimised, low energy structure for the interface. The simulations were all run for 1200 time steps or 1.2 ps. A Nose-Hoover thermostat was used to regulate the temperature during the run [26,27]. The resulting solvent/ metal interface structures established from AIMD simulations were then fully optimised using the conjugate gradient methods until the forces on all of the atoms were all less than 0.05 eV/Å. The simulations represent a very simplified model of the solvent/metal interface carried out at 0 K. They do not capture the dynamic changes in the solvent structure that is present under actual catalytic conditions or the effects of temperature as this would require hundreds of thousands of ab initio molecular dynamics simulations carried out to long times to provide the appropriate sampling which is well beyond what is currently possible. The simulations thus provide what may be a first-order effect that captures the role of explicit solvent but does not include the effects of dynamics or temperature.

The diffusion of MEK, IPA and water in IPA/water/MEK mixtures was studied using classical molecular dynamics (MD) as implemented in the Discover module of Materials Studio [28]. The MD simulations were performed on a system consisting of 64 water (for pure water) molecules in a cubic simulation cell with each side equal to 12.74 Å, which yielded liquid densities of 0.925 g/cm³ for water at 298 K. NVT simulations were carried out with periodic boundary conditions at 293.15 K in this work. Again the Nose-Hoover algorithm was used to maintain the temperature at the specified set point [26,27]. All the simulations were run for 10,000 time steps with each time step of 1 fs. Diffusion coefficients were obtained by calculating the mean squared displacements (MSD) from the simulations using the Einstein relation [29]:

$$D = \frac{1}{6t} \left\langle \left[r(t) - r(0) \right]^2 \right\rangle \tag{1}$$

where r(t) denotes the coordinates of the centre-of-mass of the molecules at time (t).

3. Results and discussion

As shown in Table 1, tests using a range of four different solvents with 5 wt% Ru/SiO_2 at 303.15 K and 1400 rpm demonstrate

Table 1

Comparison of reaction rate at 303.15 K, 3 bar H_2 and 1400 rpm using 5 wt% Ru/SiO₂ (^a measured at 298.15 K).

Rate (mol min ⁻¹ g ⁻¹) $ imes 10^4$		Dielectric constant	
Water	31.90	76.7	
IPA	4.55	19.9 ^a	
Methanol	0.95	31.6	
Heptane	1.25	1.9	

a significant variation in initial rate with water clearly producing a value over 33 times larger than that observed in methanol. Such results indicate that under the conditions used here no correlation between the dielectric constant and initial rate exists. While it cannot be guaranteed that these experiments were carried out in the kinetic regime, the fact that water has both the highest rate and lowest hydrogen gas solubility suggests that removal of mass transfer resistance, as will be demonstrated later, would only exaggerate this difference further.

When water/IPA mixtures of varying mole fractions were tested as solvents in the hydrogenation of MEK using 5 wt% Ru/SiO₂, the results showed that the observed rate increased with water mole fraction (x_{H2O}), until a maximum was attained after which it decreased until $x_{H2O} \approx 0.9$ when it again started to increase (Fig. 1).

This trend was confirmed at two different reaction conditions and it is worthy of note that a similar trend was observed by Hu et al. for the hydrogenation of 2-butyne-1,4-diol using the same solvent mixture [30]. Again the mixture dielectric constant cannot be used to correlate the rate behaviour as it is known to decrease linearly with increasing IPA concentration [31].

3.1. Gas-liquid mass transfer

As mentioned previously, the observed effect may be due to external and/or internal mass transfer limitations and hence these must be taken into consideration. Estimation of the gas-liquid mass transfer efficiency (η_{G-L}) can be expressed as:

$$\eta_{G-I} = 1 - \mathsf{Ca}_{G-L} \tag{1}$$

where Ca_{G-L} is the Carberry number for gas–liquid mass transfer which is defined as the ratio between the observed reaction rate and the maximum transfer rate both based on the liquid volume. This value is determined from the measured volumetric gas–liquid



Fig. 1. Reaction rates for MEK hydrogenation in different water/IPA mixtures at ♦ 333.15 K, 3 barg ■ 303.15 K, 1 barg (on secondary axis).

mass transfer coefficients ($k_L a$) obtained via the pressure step method and the hydrogen solubility [32,33]. While it can be seen that there is a marked increase in the $k_L a$ at $x_{H2O} > 0.50$ it decreases sharply as $x_{H2O} \rightarrow 1$, (Fig. 2). A similar effect of IPA addition to water on bubble size was observed by Hu et al. [30]; namely a minimum bubble diameter was observed at $x_{H2O} \sim 0.98$.

Hu et al. attributed this observation to a surfactant type effect with preferential adsorption of alcohol or diol at the gas-liquid interface at low concentrations. It was considered that the hydrophobic organic parts were directed into the gas phase with the hydrophilic OH groups being directed into the aqueous phase resulting in polarisation of the interface which hindered drainage/rupture of the film separating two bubbles [30]. This indicates that the changes in bubble size, which directly relate to the mass transfer rate, would be stronger functions of the surface excess energy and solution viscosity rather than the traditional Weber numbers used to estimate mean bubble diameters. Using the data published by Park et al. these can be compared with the $k_l a$ values, and as shown in Fig. 2 a reasonable correlation is observed [31]. However, when these values were used to estimate the gas-liquid mass transfer efficiency using the methods reported by Dietrich et al., all values for the mixed water/IPA system were greater than 95% except for the pure water system which yielded a value of 89% (Table 2) thereby indicating that external gas to liquid mass transfer did not account for the observed rate trends [32].

3.2. Liquid-solid mass transfer

Fishwick et al. showed that calculation of liquid to solid mass transfer rate is complicated by large local differences in the particle slip velocities within the reactor [34]. However, the liquid to solid Carberry number may be used to estimate such resistances [31]. Here calculation of the liquid–solid mass transfer coefficient, k_Ls , is estimated *via* the dimensionless Sherwood number which is it-self calculated for laboratory stirred tank reactors using the following correlation [35]

$$Sh = 2 + 0.4Re^{1/4}Sc^{1/3}$$
(2)

with the dimensionless Reynolds and Schmidt numbers calculated using Eqs. (3) and (4), respectively.

$$\operatorname{Re} = \frac{d_i^2 N \rho}{\mu} \tag{3}$$

$$Sc = \frac{\mu}{\rho D}$$
(4)



Fig. 2. Volumetric mass transfer coefficient for water/IPA mixtures. All have 0.33 mol l^{-1} of MEK except x_{H20} = 1.0.

Table 2

Calculated effectiveness factors fo	5%	Ru/SiO2.
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$x_{\rm H2O}$	η_{G-L}	$\eta_{L-S}(H_2)$	η_{L-S} (MEK)	$\eta_{pore} \left(\mathrm{H}_{2} \right)$	η_{pore} (MEK)
0	1.00	1.00	1.00	0.86	0.98
0.12	0.99	1.00	1.00	0.59	0.94
0.40	0.98	1.00	1.00	0.33	0.90
0.64	0.98	0.99	1.00	0.21	0.91
0.80	0.97	0.99	1.00	0.15	0.91
0.92	0.96	0.99	1.00	0.11	0.92
0.99	0.89	0.98	1.00	0.08	0.90

With 1% Ru/SiO₂, all transport processes had calculated effectiveness factors >0.95.

Prior to estimating the mass transfer rate, one must have knowledge of both the bulk diffusion coefficient as well as hydrogen solubility in the mixed solvents. Here the hydrogen concentration in water/IPA mixtures was evaluated from the data and equations given by Nischhenkova [36] while the Wilke–Chang correlation [37] was used for hydrogen diffusivity estimation in water and the Schiebel equation [38] for diffusivity in IPA. For mixed solvents the correlation developed by Perkins and Geankoplis [39] was used, where the viscosity of the mixture was calculated from the equation developed by Kendall and Monroe [40]. Despite the approximations used for bulk diffusivity, the estimated and calculated data were both used to determine the liquid–solid Carberry number which was then utilised to estimate the liquid–solid mass transfer efficiency according to Eq. (5)

$$\eta_{L-S} = \left(1 - \operatorname{Ca}_{L-S}\right)^n \tag{5}$$

In each case, the external mass transfer efficiencies were shown to be ≥ 0.98 for all solvent compositions when both H₂ and MEK (Table 1) are treated as the limiting species and therefore liquid-solid mass transfer was not considered to be limiting in this system.

At present we are not aware of any experimental results for hydrogen diffusivity in mixed solvents which could be used to help validate the aforementioned empirical equations; however, such a comparison can be made for 2-butanone using the data measured by PFG-NMR across the entire solvent composition range, as shown in Fig. 3. A minimum in the rate of diffusion of 6.59×10^{-10} m² s⁻¹ is seen at ~85 mol_{H20}%. This minimum implies that molecular mobility is hindered and hence liquid structuring is enhanced at this concentration. The previously reported diffusion coefficient of 2propanol in the binary 2-propanol/water system follows a similar



Fig. 3. Diffusion coefficient of 2-butanone (0.33 mol l^{-1}), in 2-butanone/2-propanol/water mixtures at 303.15 K using PFG-NMR, MD calculations and literature correlations.

trend [41]. Comparing the measured data to calculated values (also shown in Fig. 3) a significant difference between the calculated and the experimental data is evident. However, even when using these calculated data, the results still indicate that liquid–solid mass transfer for MEK was not limiting. If similar errors are imposed on the hydrogen diffusivity, the mass transfer efficiency is reduced but is still high enough for it to be considered as not limiting. Therefore, while in this case it is unlikely that liquid–solid diffusion is important, this analysis does highlight deficiencies in the empirical correlations employed here for diffusivity estimation.

There are of course a number of alternative correlations which could be used to estimate the diffusivity in pure or mixed solvents, although these will not be reported here as even an order of magnitude change here in diffusivity estimates does not alter the conclusion that external mass transfer rates are not limiting in this case. The diffusivity of MEK in different ternary mixtures of IPA. water and MEK was, however, estimated using classical molecular dynamics simulations. The compositions of the ternary mixtures were varied by changing the relative number of molecules in the system. Here we considered ternary mixtures with 0% (IPA 92.7% and MEK 7.3%), 41.2% (IPA 51.5% and MEK 7.3%), 74.2% (IPA 18.5% and MEK 7.3%) and 96.9% (MEK 3.1%) water (mole fractions). The number of water, IPA and MEK molecules per unit cell in these systems were chosen as (0:38:3), (17:21:3), (30:8:3) and (62:0:2), respectively. The diffusivity of MEK in these mixtures was then calculated based on the mean squared displacement of MEK molecules over 10 ps. As shown in Fig. 3, the diffusivity of MEK in the ternary solution changes with the composition. It can be observed that the molecular dynamics results for diffusivity are in agreement, at least qualitatively, with the PFG-NMR results and that using this method also suggests a minimum diffusivity of MEK when $x_{\rm H2O}$ is close to 0.74.

3.3. Internal mass transfer

In Fig. 4, tests with varying catalyst particle sizes showed that the observed reaction rate increased with decreasing particle size, inferring pore diffusion limitations. Here the particle size was determined using known sieve fractions and only the initial rate is reported as it is known that the particle size reduces during the experiment due to the shear forces from the impeller.



Fig. 4. Observed initial rate with varying particle size.

As it is known that the catalyst is not poisoned by product, the Weisz-Prater criteria were employed to calculate the effectiveness factor, and subsequently used to give an estimate of the true reaction rates [42]. In general if the calculated value of $\phi_{WP} \ll 1$, then the reaction is absent of internal mass transfer limitations. This value changes depending on the order of the reaction and a very good review of this method and its application is given by Mukherjee and Vannice [43]. Using the calculated efficiencies it is possible to modify the observed reaction rates and to therefore estimate a 'true' rate which is free from mass transfer effects. The result of this manipulation is shown in Fig. 5 where it can be seen that the corrected reaction rate now increases with x_{H20}. This increase proceeds linearly up to $x_{H2O} \approx 0.8$, after which it increases much more rapidly until x_{H20} = 1.0. It is possible that the increasing rate over the lower water concentrations could now be attributed to previous discussions, e.g. changes in the bulk dielectric constant or related to changes in the adsorption equilibria on the catalyst surface. Obviously the change at $x_{\rm H2O} \approx 0.8$ suggests that water is playing a key role in enhancing the reaction rate above this concentration. It should be noted that the result of this manipulation is, in this case, much more sensitive to estimated values of the diffusion constant and particle size. For example a 20% increase in the diffusion coefficient will contribute to approximately a 10% increase in the rate, whereas a 20% increase in the particle diameter will result in a 17% decrease in the rate (Note, these sensitivities are evaluated when the efficiency was originally estimated at 24%). This sensitivity is of course one of the main reasons for operating in the mass transfer free region; and therefore, in order to confirm that this effect was not an artefact of introducing the efficiency correction, the reactions were repeated using a catalyst with a lower loading and smaller particle size, i.e. 1% Ru/SiO₂ and 20 µm. In this case all the calculated mass transfer limitations, using the above correlations, were negligible and this catalyst showed the trend directly. It can also be observed that the 1% catalyst was an order of magnitude slower than the 5% catalyst, which may be attributed here to differences in the dispersion or errors in the efficiency calculations. Transmission electron microscopy (TEM) studies were performed to obtain Ruthenium particle size distribution data for both 1% and 5% Ru/SiO₂ catalysts. This TEM data collected for both catalysts showed that the 1% Ru/SiO₂ catalyst has a smaller ruthenium particle sizes (\sim 1.5 nm) with a higher metal dispersion than the 5% Ru/SiO₂ catalyst which showed average particle sizes of \sim 3 nm, as shown in Fig. 6. The above clearly



Fig. 5. T = 303.15 K, P = 1 barg, corrected rate for 5% Ru/SiO₂ using calculated internal mass transfer effectiveness for hydrogen as well as the uncorrected for 1% Ru/SiO₂.

shows that when operating under mass transfer limitations the observed rate is a non-linear function of solvent composition. Even when removing such mass transfer limitations, through estimation of the efficiencies or through choice of catalyst, there still remains an inflexion in the rate at high water concentrations. The change in rate at ≈ 0.85 mole fraction of water suggests a structural change in the system as has been previously reported using THz-TDS data and 2-proponol/water mixtures [41]. Herein, the measured THz-TDS absorption coefficient, shown in Fig. 7a, is compared with the rate of reaction. A clear correlation between reaction rate and spectroscopic data is observed. The absorption coefficient as measured is directly related to hydrogen-bond dynamics and is considered as a probe of the structure of the solvent. Qualitatively it is apparent that above 85-90 mol_{H20}% the alcohol-water mixture rapidly tends to the absorption coefficient and hence structure of bulk water. This can be ascribed to the fact that below this concentration, water molecules are largely accounted for within 2-propanol/water networks, with increasing bulk-like water above this concentration.

It is valid to consider whether studies on alcohol/water mixtures have a direct relevance for catalytic systems when studied in the absence of the reactant molecules. As we and others have shown, the addition of a small concentration of alcohol into bulk water dramatically alters the properties of the liquid. The addition of reactant could therefore feasibly have a similar influence on alcohol/water mixtures. In order to address this, we have studied the influence of the addition of 0.33 mol l^{-1} 2-butanone to 2-propanol water mixtures across the entire composition range. It should be noted that 2-butanone is a hydrogen-bond acceptor only, unlike 2-propanol and water which are both hydrogen-bond acceptors and hydrogen-bond donors. Fig. 7b shows the relative absorption coefficient of the ternary mixture: a greater relative absorption coefficient indicates more retarded rotational dynamics and an increase in structuring. Here the maximum relative absorption coefficient is shifted to a slightly lower value ~85 - mol_{H20} % than that observed in the absence of MEK [41] and therefore it can be concluded that the existence of 2-butanone does not influence the structures of such mixtures significantly; however, an increase in the magnitude of the relative absorption with respect to the binary mixture is observed. This indicates that the presence of 2-butanone further hinders the rotational dynamics of the system. That 2-butanone interacts with water but not with 2-propanol is confirmed by the fact that the relative absorption coefficient is zero at 0% water but non-zero at 100% water (with 0.33 mol l⁻¹ 2-butanone).

It is clear that the concentration at which the maximum in the relative absorption coefficient is observed is not only coincident with rapid acceleration in the reaction rate (Fig. 5) but also with well-established excess thermodynamic properties of IPA/H₂O mixtures. For instance, the negative excess enthalpy, i.e. excess with respect to an ideal non-interacting mixture, reaches a maximum at $x_{H2O} \sim 0.90$. This effect is due to the presence of hydrogen-bonding interactions between the water and alcohol molecules, which in turn influence the structural dynamics of the solvent.

The above results clearly show that water has a significant effect on the reaction rate. For the data determined using 5% Ru/SiO₂ at 303.15 K and 1 bar of hydrogen this rate increased by \approx 7 (pre-correction) to \approx 75 (post-correction) times that of the IPA solvent. This is much larger than the case of the 1% catalyst which only showed an order of magnitude increase in reaction rate and as discussed indicates that the efficiency corrections used here are likely to have over predicted the 'real' reaction rate. Nevertheless, there is a clear increase when using water and this increase appears to correlate with bulk solvent structure. However, if one normalises the observed reaction rate to the hydrogen concentration (assuming first order, as identified for the water case), this difference increases further with the 1% Ru/SiO₂ (i.e. non-modified



Fig. 6. HR-TEM images and particle size distribution of (a) 1% Ru/SiO₂ and (b) 5% Ru/SiO₂ catalysts.



Fig. 7. (a) Absorption coefficient of 2-propanol/water mixtures at 1 THz [41]. (b) Relative absorption coefficient of 2-butanone/2-propanol/water mixtures (303 K) at 1 THz as evaluated from THz-TDS measurements.

rate) now giving a normalised rate which is 63 times higher in water when compared to IPA. Such a significant increase in reaction rate necessitates further investigation on how such structural differences may relate to the observed rate changes between systems.

3.4. Role of solvent

In order to begin to understand the influence of water on the increased rates of reaction, we carried out density functional theoretical calculations to model the adsorption and hydrogenation of MEK over Ru(0001) in the vapour phase as well as in 2-propanol and aqueous solvents. A detailed description of these and related simulations is given elsewhere [44–46].

MEK hydrogenation follows Langmuir–Hinshelwood kinetics where both MEK and hydrogen chemisorb on the metal surface and react *via* a series of hydrogen addition steps through a Horiuti–Polanyi like mechanism [47]. MEK adsorbs atop of a Ru atom of the Ru(0001) surface through its oxygen atom in an η^1 configuration (Fig. 8a) with an adsorption energy of 33 kJ mol⁻¹. The hydrogenation of MEK can then proceed *via* two different pathways.

In the first path (hydroxy route), an adsorbed hydrogen atom adds to the oxygen of MEK to form a hydroxybutyl intermediate (Fig. 9b) which is bound di- σ to the surface through its carbon and oxygen atoms (Fig. 8b). This reaction proceeds *via* the addition of hydrogen to the Ru–O bond in the three centre transition state as depicted (Fig. 9a). The Ru–O bond increases from 2.13 Å in MEK to 2.26 Å in the transition state as O–H bond begins to form (1.40 Å). The activation barrier for this step was calculated to be 64 kJ mol⁻¹ (Table 3a). The subsequent hydrogenation of the hydroxybutyl intermediate to form 2-butanol (Fig. 8d) was found have a barrier of 72 kJ mol⁻¹. The transition state for this step involves the addition of hydrogen to the Ru–C bond as is shown in Fig. 9d.

In the second path (alkoxy route), hydrogen first adds to the carbon atom to form the 2-butoxy intermediate (Fig. 9c) which is bound to a three-fold hollow site through its oxygen atom (Fig. 8c). The transition state for this step involves the insertion

of hydrogen into the Ru-C bond as is shown in Fig. 9c. The transition state is very similar to that shown in Fig. 9d for the C-H bond formation in the hydroxy route. The activation barrier for this step was calculated to be 58 kJ mol⁻¹ (Table 3b). The subsequent hydrogenation of the butoxy intermediate to form 2-butanol proceeds via the addition of hydrogen to the Ru-O bound. Again the transition state for this reaction which is shown in Fig. 9d is very similar to that found for the first hydrogenation step in the hydroxy route (Fig. 9a) as both involve the formation of an O-H bond. The activation barrier for this step, however, was calculated to be 124 kJ mol⁻¹ which is significantly higher than the other three elementary steps discussed; as such, this may limit the reaction rate. While the activation barrier for the first hydrogenation step in the alkoxy route is lower than that found in the hydroxy route, the second step in the alkoxy route is significantly higher than that in the hydroxy route. We carried out kinetic Monte Carlo simulations for the hydrogenation of MEK over Ru in the vapour phase and found that the product (2-butanol) is mainly formed via the alkoxy route [44]

In the presence of the solvent, the hydroxy route was found to be more favourable than that the alkoxy route. The structures for all the reactants, products and transition states were calculated to be very similar to those found for the vapour phase reaction. MEK adsorbs at the metal-water interface by displacing a water molecule from the metal surface. Two of the water molecules within the first solvation shell of the adsorbed MEK form hydrogen bonds with the MEK (Fig. 10a). Similar to the results in the vapour phase, the hydroxybutyl intermediate, formed by the reaction of MEK and hydrogen, binds through the carbon atom of its initial carbonyl group. The hydroxyl group that results is directed towards the solution phase where it is stabilised by forming hydrogen bonds with water molecules in solution, as is shown in Fig. 10b. The Ru–O bond that forms between the hydroxybutyl and the Ru surface is 2.19 Å as compared to 2.06 Å for MEK which indicates a stronger interaction of the intermediate with the aqueous solvent than with the surface [45].

The accessibility of the hydroxyl group to the bulk solvent allows it to participate in hydrogen bonding with a water molecule in the bulk solution and leads to extra stabilisation over the



Fig. 8. DFT-optimised adsorption configurations for (a) MEK (b) hydroxybutyl intermediate (c) butoxy intermediate and (d) 2-butanol over Ru(0001) in the vapour phase.



Fig. 9. DFT-calculated transition state structures for the hydrogenation of (a) MEK to form the hydroxybutyl intermediate, (b) the hydroxybutyl intermediate to butanol, (c) MEK to butoxy intermediate and (d) the butoxy intermediate to 2-butanol over Ru(0001) in the vapour phase.

Table 3a

DFT predicted reaction energy and activation barriers for the hydrogenation of MEK to hydroxybutyl and hydroxybutyl to 2-butanol in vapour, water and IPA.

Solvent	$R_1R_2C^*=O^*+H^*\rightarrow R_1R_2C^*{-}OH$		$R_1R_2C^*{-}OH+H^*\rightarrow R_1R_2CH{-}O^*H$	
	$\Delta E_{\rm rxn}$ (kJ/mol)	$E_{\rm act}$ (kJ/mol)	$\Delta E_{\rm rxn}$ (kJ/mol)	E _{act} (kJ/mol)
Vapour	21	64	-18	72
Water	-23	20	-20	68
IPA	-16	32	-20	70

 $R_1=CH_3CH_2, R_2CH_3. \label{eq:R1}$

Table 3b

DFT predicted reaction energy and activation barriers for the hydrogenation of MEK to
butoxy and butoxy to 2-butanol in vapour, water, and IPA.

Solvent	$R_1R_2C^*=O^*+H^* \rightarrow R_1R_2CH{-}O^*$		$R_1R_2CH{-}O^*+H \rightarrow R_1R_2CH{-}O^*H$	
	$\Delta E_{\rm rxn}$ (kJ/mol)	E _{act} (kJ/mol)	$\Delta E_{\rm rxn}$ (kJ/mol)	E _{act} (kJ/mol)
Vapour	-47	58	50	123
Water	-47	58	4	115
IPA	-42	62	6	116

 $R_1=CH_3CH_2, R_2CH_3\textbf{.}$



Fig. 10. DFT-optimised adsorption configurations for (a) MEK, (b) hydroxybutyl intermediate, (c) butoxy intermediate and (d) 2-butanol over Ru(0001) in the aqueous phase. For clarity, the hydrogen atom involved in hydrogenation has been shown in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 11. DFT-calculated transition state structures for the hydrogenation of (a) MEK to hydroxybutyl intermediate, (b) the hydroxybutyl intermediate to 2-butanol, (c) MEK to butoxy intermediate and (d) the butoxy intermediate to 2-butanol over Ru(0001) in the aqueous phase. For clarity, the hydrogen atom involved in hydrogenation has been shown in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reactant state (MEK). In the reaction to form the hydroxybutyl intermediate, the transition state takes on the classic three centre form with O–H, Ru–O and Ru–H bond lengths of 1.37, 2.18 and 1.7 Å, respectively. Both the hydrogen and the oxygen in the transition state (Fig. 11a) interact with water molecules within their local solvation sphere (including water molecules at the surface as

well as in the bulk solvent) which lowers the activation barrier to 20 kJ mol⁻¹ from 64 kJ mol⁻¹ in the vapour phase reaction. The transition state for the subsequent hydrogenation of the hydroxybutyl intermediate to form 2-butanol in water, which is shown in Fig. 11b, was also very similar to that in the vapour phase. The activation barrier in the solution phase was calculated to be



Fig. 12. A snapshot from *ab initio* molecular dynamics simulation of proton diffusion in pure water. Two water molecules participate in formation of an $H_5O_2^+$ intermediate as proton shuttles through the hydrogen-bonding network.

 65 kJ mol^{-1} which is also lower than that reported above for the vapour phase (72 kJ mol}^{-1}).

The hydrogenation of MEK to form the butoxy intermediate involves the formation of a C-H bond in the transition state (Fig. 11c) which is much less polar than the formation of the O-H bond for the formation of the hydroxybutyl. As such, there is far less hydrogen-bonding stabilisation of the transition state to form the butoxy as compared to that for the hydroxybutyl. The activation barrier for this step in presence of the water was calculated to be 58 kJ mol $^{-1}$, which is identical to that found for the vapour phase reaction. The transition state for the subsequent hydrogenation of the butoxy intermediate in water was calculated to be 120 kJ mol⁻¹ which is very similar to the value of 124 kJ mol⁻¹ calculated for the vapour phase reaction (Fig. 12d). Unlike the adsorbed MEK, the alkoxide reactant is already quite polar and stabilised by water in the reactant state. The number of hydrogen bonds with water on the surface and in solution remains the same between the reactant and the transition state. As such, there is only a very small stabilisation (4 kJ mol⁻¹) of the transition over the reactant state due to the presence of water.

A comparison of both mechanisms in the vapour and the solution phase reveals that the presence of water favours the formation of the O–H bond formation over that of the C–H bond, especially in the hydroxy path. While both the alkoxy and hydroxy routes have similar activation barriers for the reactions carried out in the vapour phase, the hydroxy path is clearly favoured over the alkoxy route when the reactions are carried out in solution as a result of the stronger stabilisation of the lower barrier to form the O–H bond over the C–H bond and the increased stability of the hydroxybutyl intermediate over the butoxy intermediate.

Previously we have shown that the apparent barriers for the hydrogenation of ketones and aldehydes to alcohols can be described by the rate which depends on the intrinsic hydrogenation of either the hydroxyalkyl or the alkoxide intermediates [44]. The results presented here for both mechanisms reveal that water clearly lowers the effective barrier for the hydrogenation of MEK. The solution phase also induces a change in the governing reaction path over that found in the vapour phase.

The same reaction steps were studied using IPA as a solvent. The calculated activation barriers for the first hydrogenation step in IPA for the hydroxy and alkoxy mechanisms were calculated to be 32 kJ mol^{-1} and 68 kJ mol^{-1} , respectively. As observed in the case of water, the activation barrier is lower for the hydroxy route as compared to the vapour phase reaction but there is very little difference in barrier for the alkoxy route. The relative stabilisation of transition state for the formation of hydroxybutyl intermediate in presence of IPA is not as strong as in the case of water. Thus, the

activation barrier for this step is lower in water as compared to IPA by 12 kJ mol⁻¹. This is the result of the loss of an addition hydrogen bond with the solution phase. A more detailed description of the transition state structures is reported elsewhere [45]. In summary, DFT predicts that the activation barriers for hydrogenation of MEK follow the order of: vapour > IPA > water. Given that heptane is the closest representation of the vapour phase, this trend is in excellent agreement with the reported experimental data for the solvents (Table 1) particularly when normalised to hydrogen solubility. As reported here, hydrogenation rates at 303 K were found to be an order of magnitude greater in water than in IPA. While this can be attributed to the lower activation barrier for hydrogenation of MEK in water (20 kJ mol⁻¹) than IPA (33 kJ mol⁻¹), it does not, however, account for the rapid increase in reaction rate at $x_{H2O} \approx 0.8$.

In addition to dissolving molecular hydrogen, it is known that the solvent is also capable of transporting charged reaction species. The ease of transport of these species can ultimately be decisive in determining the rate of the reaction. In order to further explain the peculiar behaviour in the hydrogenation rate of MEK at higher concentrations of water (Fig. 1), we carried out ab initio molecular dynamics to monitor proton diffusivities in IPA-water solvents with different compositions ($x_{H2O} = 1$ and 0.87). Proton transfer was chosen here as a very simple probe of the diffusion of polar or ionic species in aqueous media and in addition since some hydrogenation reactions in aqueous media have been suggested to involve protons that form locally. The simulations were run out to 5 ps (using time step of 1 fs) in order to allow the proton to diffuse through the solution. It was observed that the proton readily shuttles through a chain of water molecules by forming a Zundel ion $(H_5O_2^+)$ like intermediate and a successive sequence of proton transfer steps (Fig. 12). In pure water ($x_{H2O} = 1$), the diffusivity of the proton was found to be $2\times 10^{-8}\,m^2\,s^{-1}$ which is in close agreement with other molecular dynamics and experimental studies [48]. However, in the water–IPA mixture ($x_{H20} = 0.87$) the diffusivity was found to be over 27 times lower $(7.52 \times 10^{-10} \text{ m}^2 \text{ s}^{-1})$. These simulations show that the presence of IPA disrupts the highly interconnected hydrogen-bonding network between water molecules which subsequently inhibits facile proton transport and thus lowers the diffusivity. These results indicate that proton transfer increases considerably as solvent composition changes from $x_{H2O} = 0.87$ to $x_{H2O} = 1$ and that this may significantly enhance hydrogenation activity. This is in agreement with our experimental results for the hydrogenation of MEK in mixed solvents (Fig. 1) as well as the THz-TDS data (Fig. 7).

It is clear that hydrogen-bonding structure and dynamics can play various roles in determining the catalytic behaviour of a system. The diffusion of protons through solution, a key step in catalytic hydrogenation described in the present work, and in electrocatalytic reduction reactions such as those occurring in proton exchange membrane fuel cells, is coupled to these dynamics [49,50]. Recent work has shown that the efficiency of this proton diffusion appears to be coupled to hydrogen-bonding dynamics and structure of the liquid [51,52]. This diffusion or 'proton-shuttling' is often described by the Grotthus mechanism [47], which is discussed in detail elsewhere [47,53,54]. Briefly, it involves the effective transfer of a proton through the breaking and formation of hydrogen bonds: specifically, isomerisation between H₃O⁺ and $H_5O_2^+$ which couples to hydrogen-bonding dynamics in the second solvation shell of the H₃O⁺. Recent THz-TDS studies have, however, suggested that 15 water molecules may actually be involved in the proton diffusion process [55]. Bond-order analysis of molecular dynamics simulations has shown that the timescale of this proton transfer is of the order of a few ps [56]. This timescale also corresponds to the lifetime of the alcohol and water clusters in alcohol-water mixtures observed by neutron diffraction studies [57]

and the timescale of the processes probed by THz-TDS. The structure of alcohol–water mixtures additionally dictates the diffusion of solvated electrons, a crucial step in both electrocatalytic and non-catalytic electrochemical reactions [58]. For example, aqueous solutions of methanol, ethanol, 1-propanol, 2-propanol and 1-butanol, 2-butanol and *tert*-butanol all show a maximum in the free ion yield upon irradiation at alcohol concentrations of a few mol% [54–63]. For aqueous 2-propanol, this maximum occurs at ~97 mol_{H20}% [54].

4. Conclusions

The results described herein have shown that there is a significant variation in the observed rate of the MEK hydrogenation reaction when using 5% Ru/SiO₂ in different solvents. In particular, a complex behaviour is observed for varying water/IPA mole fractions. Using experimental and estimated mass transfer rates we have shown that while gas-liquid mass transfer also varies significantly with water mole fraction, it, like the liquid-solid mass transfer, is not significant at the scale of the reactor used here. Internal mass transfer was, however, shown to be significant. Correcting the observed rate for the calculated internal effectiveness using literature correlations revealed that the rate increased as the water mole fraction increased. This was confirmed by using a lower loaded catalyst (1%), although a comparison with the 5% catalyst indicates that the mass transfer corrections used here did appear to over predict the 'true' reaction rate. Results from density functional theory calculations showed that water can significantly lower the activation energy for the reaction as compared to the reactions in isopropyl alcohol or the vapour phase, and, in addition, can alter the preferred hydrogenation mechanism. The above rationalises why water is a significantly better solvent than IPA or indeed other alcohols and alkanes. This, however, did not explain why the intrinsic rate is not ostensibly linear as a function of solvent composition, but rather goes through a sharp increase at high water concentrations (>90 mol%). For gas liquid systems, Hu et al. observed a significant effect at much lower IPA concentrations than this - a few mole% and this was explained by the surface-active behaviour of the alcohol at the gas liquid interface [30]. This explanation does not appear germane in this context. In order to explore the probable explanation, the structure of the IPA-water mixture was explored and a correlation observed but one which did not correspond completely to the composition of minimum diffusivity or azeotrope. Therefore, ab initio molecular dynamics techniques were employed which showed that water was also found to facilitate diffusion of protons as well as the diffusion of MEK demonstrating significant enhancements for concentration greater than 90% water.

The above discussions highlight the potential beneficial role of water in both lowering the activation barrier as well as increasing the proton diffusion coefficient and combined these effects appear to correlate well with the experimental data reported. However, it should also be noted that significant deactivation is observed in the presence of water [64]. At high concentrations of water, this deactivation occurs at a sufficiently fast time scale so that it should be included in any reaction model. However, it did not affect the initial rate data presented here.

The results reported herein therefore suggest that catalytic performance can be tailored through controlling the structural dynamics of the solvent, e.g. through changing composition.

Overall, this work confirms and highlights the importance of the solvent system in modifying the mass transfer, diffusion and reaction mechanism during the hydrogenation of MEK. Furthermore, it demonstrates that it is possible to link DFT calculations, spectroscopy and reaction kinetic data to better understand complex behaviour in catalytic systems.

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References

- M.H. Abraham, P. Grellier, J.M. Abboud, R.M. Doherty, R.W. Taft, Can. J. Chem. 66 (1988) 2673.
- [2] L. Gilbert, C. Mercier, in: M. Guisnet, J. Barbier, J. Barrault, G. Bouchoulo, D. Duprez, G. Pérot, C. Montassier (Eds.), Heterogeneous Catalysis and Fine Chemicals III, Elsevier, Amsterdam, 1993, p. 51.
- [3] S. Asplund, C. Fornell, A. Holmgren, S. Irandoust, Catal. Today 24 (1995) 181.
- [4] E. Toukoniitty, P. Mäki-Arvela, J. Kuusisto, V. Nieminen, J. Päivärinta, M. Hotokka, T. Salmi, D.Y. Murzin, J. Mol. Catal. A: Chem. 192 (2003) 135.
- [5] S. Mukherjee, A. Vannice, J. Catal. 243 (2006) 108.
- [6] S. Gómez-Quero, E. Díaz, F. Cárdenas-Lizana, M. Keane, Chem. Eng. Sci. 65 (2010) 3786.
- [7] B. Hu, R.P. Fishwick, A.W. Pacek, J.M. Winterbottom, J. Wood, E.H. Stitt, A.W. Nienow, Chem. Eng. Sci. 62 (2007) 5392.
- [8] J. Wood, J.A. Bennett, N.J. Creamer, L.E. Macaskie, L. Bodeness, in: 8th World Congress of Chem. Eng., Montreal, Canada, 2009.
- [9] J. Masson, P. Cividino, J. Court, Appl. Catal. A: Gen. 161 (1-2) (1997) 191.
- [10] R.A. Rajadhyaksha, S.L. Karwa, Chem. Eng. Sci. 41 (7) (1986) 1765.
- [11] U.K. Singh, M.A. Vannice, Appl. Catal. A: Gen. 213 (2001) 1.
- [12] L. Vanoye, M. Zanota, A. Desgranges, A. Favre-Reguillon, C. De Bellefon, Appl. Catal. A: Gen. 394 (2011) 276.
- [13] P. Kluson, L. Cerveny, Appl. Catal. A: Gen. 128 (1995) 13.
- [14] M. Hronec, Z. Cvengrošová, M. Králik, G. Palma, B. Corain, J. Mol. Catal. A: Chem. 105 (1996) 25.
- [15] P.D. Vaidya, V.V. Mahajani, Chem. Eng. Sci. (60) (2005) 1881.
- [16] J. Weissenrieder, A. Mikkelsen, J.N. Andersen, P.J. Feibelman, G. Held, Phys. Rev. Lett. 93 (19) (2004) 196102.
- [17] S.K. Desai, M. Neurock, Phys. Rev. B 68 (7) (2003) 075420.
- [18] J.E. Tanner, J. Chem. Phys. 52 (1970) 2523.
- [19] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864 LP.
- [20] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558.
- [21] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133 LP.
- [22] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
- [23] D. Vanderbilt, Phys. Rev. B 32 (1985) 8412.
- [24] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) LP 5188.
- [25] G. Mills, H. Jonsson, G.K. Schenter, Surf. Sci. 324 (1995) 305.
- [26] W.G. Hoover, Phys. Rev. A 31 (1985) 1695.
- [27] S. Nose, J. Chem. Phys. 81 (1984) 511.
- [28] Materials Studio, v4.4.0.0 ed. Accelrys Software Inc., San Diego, CA, 2008.
- [29] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, Oxford, 1989.
- [30] B. Hu, A.W. Nienow, A.W. Pacek, E.H. Stitt, Ind. Eng. Chem. Res. 46 (13) (2007) 4451.
- [31] J.G. Park, S.H. Lee, J.S. Ryu, Y.K. Hong, T.G. Kim, A.A. Busnaina, J. Electrochem. Soc. 153 (9) (2006) G811.
- [32] E. Dietrich, C. Mathieu, H. Delmas, J. Jenck, Chem. Eng. Sci 47 (1992) 3597.
- [33] F. Kapteijn, E. Crezee, B.W. Hoffer, R.J. Berger, M. Makkee, J.A. Moulijn, Appl. Catal. A: Gen. 251 (2003) 1.
- [34] R.P. Fishwick, J.M. Winterbottom, E.H. Stitt, Catal. Today 79 (2003) 195.
- [35] Y. Sano, N. Yamaguchi, T. Adachi, J. Chem. Eng. Jpn. 7 (1974) 255.
- [36] L.G. Nischhenkova, M.V. Ulitin, V.N. Gorelov, Izv. Vys. Ucheb. Zaved. Khim. I Khim. Tekhnol. 33 (1990) 22.
- [37] C.R. Wilke, P. Chang, Am. Inst. Chem. Eng. J. 1 (1955) 264.
- [38] E. Scheibel, Ind. Eng. Chem. 46 (1954) 2007.
- [39] L.R. Perkins, C.J. Geankoplis, Chem. Eng. Sci. 24 (1969) 1035.
- [40] J. Kendall, K. Monroe, J. Am. Chem. Soc. 39 (1917) 1787.
- [41] J. McGregor, R. Li, J.A. Zeitler, C. D'Agostino, J. Collins, M.D. Mantle, H.G. Manyar, J.D. Holbrey, T. Youngs, C. Hardacre, E.H. Stitt, L.F. Gladden, Phys. Chem. Chem. Phys., submitted for publication.
- [42] P.B. Weisz, C.D. Prater, Adv. Catal. 6 (1954) 144.
- [43] S. Mukherjee, M.A. Vannice, J. Catal. 243 (2006) 108.
- [44] N.K. Sinha, M. Neurock, J. Catal., submitted for publication.
- [45] N.K. Sinha, M. Neurock, Chem. Cat. Chem. submitted for publication.

- [46] N.K. Sinha, Ph.D. Thesis, Theoretical Insights into the Influence of Solvent on Heterogeneous Catalytic Hydrogenation and Hydrogenolysis Reactions, University of Virginia, 2011.
- [47] J. Horiuti, M. Polanyi, Trans. Farad. Soc. 30 (1934) 1164.
- [48] B. Mauro, I. Tamio, T. Kiyoyuki, Chem. Phys. Chem. 6 (2005) 1775.
- [49] M.J. Janik, C.D. Taylor, M. Neurock, Top. Catal 46 (3-4) (2007) 306.
- [50] M.J. Janik, C.D. Taylor, M. Neurock, J. Electrochem. Soc. 156 (1) (2009) B126.
- [51] N. Agmon, Chem. Phys. Lett. 244 (5) (1995) 456.
- [52] C.D. Taylor, M. Neurock, Curr. Opin. Solid State Mater. Sci. 9 (1-2) (2005) 49. [53] D. Marx, M.E. Tuckerman, J. Hutter, M. Parrinello, Nature 397 (6720) (1999)
- 601. [54] M. Tuckerman, K. Laasonen, M. Sprik, M. Parrinello, J. Phys. Chem. 99 (16) (2002) 5749.
- [55] K.J. Tielrooij, R.L.A. Timmer, H.J. Bakker, M. Bonn, Phys. Rev. Lett. 102 (19) (2009) 198303.

- [56] H. Lapid, N. Agmon, M.K. Petersen, G.A. Voth, J. Chem. Phys. 122 (2005) 1.
- [57] L. Dougan, S.P. Bates, R. Hargreaves, J.P. Fox, J. Crain, J.L. Finney, V. Reat, A.K. Soper, J. Chem. Phys. 121 (13) (2004) 6456.
- [58] J. Cygler, G.R. Freeman, Can. J. Chem. Revue Can. Chimie 62 (7) (1984) 1265. [59] A.D. Leu, K.N. Jha, G.R. Freeman, Can. J. Chem. - Revue Can. Chimie 60 (18) (1982) 2342.
- [60] Y. Maham, G.R. Freeman, J. Phys. Chem. 89 (20) (1985) 4347.
- [61] Y. Maham, G.R. Freeman, J. Phys. Chem. 91 (6) (1987) 1561.
- [62] P.C. Senanayake, G.R. Freeman, J. Chem. Phys. 87 (12) (1987) 7007.
- [63] Y. Maham, G.R. Freeman, Can. J. Chem. Revue Can. Chimie 66 (7) (1988) 1706.
 [64] H.G. Manyar, D. Weber, H. Daly, J.M. Thompson, D.W. Rooney, L.F. Gladden, E.H. Stitt, J.J. Delgado, S. Bernal, C. Hardacre, J. Catal. 265 (1) (2009) 80.